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(54) Coating process for aluminium

(57) An aluminium metal surface as treated by sequentially contacting the surface with an aqueous acidic treatment solution containing hafnium, zirconium and/or titanium ions, fluoride ions, a tannin compound and a sequestering agent and then treating the metal surface with a solution comprising a polyphenolic compound or acid salt thereof.

SPECIFICATION

Coating process for aluminium

5 The present invention relates to the treatment of aluminium metal surfaces to produce an adherent corrosion-resistant coating thereon which is receptive to organic or siccative coatings. 5

For environmental reasons it is desirable to substitute conventional chromium and phosphate containing treatment chemicals in the metal treatment industry with alternative compounds devoid of chromium.

10 U.S. 4,338,140 describes an aqueous acidic composition which provides improved corrosion resistance to a metal, for example, ferrous, zinc or aluminium. The composition contains dissolved hafnium and/or zirconium, fluoride, preferably a vegetable tannin compound, and optionally phosphate ions. 10

U.S. 4,457,790 relates to the treatment of metal surfaces with a dilute solution of a poly-alkenylphenol derivative or an acid salt of a poly-alkenylphenol derivative.

15 In the treatment of extruded aluminium surfaces, it is important that the surfaces be provided with a coating which provides protective corrosion resistance while also being adherent and receptive to subsequently applied finishes such as paint, varnish, lacquer, etc., which may be later applied to the coated surface. The qualities required of a coating are many and vary in importance depending on the end use to which the coated article is put. Of concern are adhesion of the coating to the metal surface and of a subsequently applied finish to the coated surface, corrosion resistance of the coated but unfinished surface and of the finished surface, the colour or colourless nature of the coating, the uniformity of the coating, the coating thickness required to obtain minimum acceptable qualities, the formability of the coated metal article, and the etching or other distortion of the metal surface appearance. 15 20

The present invention provides a coated aluminium surface which has excellent corrosion resistance and paint adhesion characteristics and, generally, provides a coating of surprisingly excellent quality when viewed from the above-recited concerns. 25

All parts and percentages herein are by weight unless otherwise indicated.

In accordance with the invention an aluminium metal surface, especially an extruded aluminium metal surface, is treated by sequentially contacting the surface with

30 (1) an aqueous acidic treatment solution comprising effective amounts of dissolved metal ions selected from the group consisting of hafnium, zirconium, titanium and mixtures thereof, fluoride ions, phosphate ions, a bath soluble vegetable tannin compound, and a sequestering agent; 30

(2) a post-treatment solution comprising an effective amount of a soluble or dispersible treatment compound selected from polymers of formula 1, acid salts thereof, and mixtures thereof, wherein R_1 through

35 R_3 are hydrogen or an alkyl group having from 1 to about 5 carbon atoms; each Y is hydrogen, Z, $CR_4R_5OR_6$, CH_2Cl , or an alkyl or aryl group having from 1 to 18 carbon atoms; 35

Z is a group of formula II, and wherein the groups R_4 to R_{10} are each hydrogen, or an alkyl, aryl, hydroxy-alkyl, amino-alkyl, mercapto-alkyl or phospho-alkyl moiety, and wherein the groups R_4 to R_{10} are

40 each of carbon chain lengths below a length at which the compound (or its acid salt) is not soluble or dispersible; and n is at least 2 but below a number at which the polymer or its acid salt is not soluble or dispersible. 40

The amount of each of the components in the first solution will be sufficient to provide, together, corrosion resistant adherent coating on the surface.

The process is especially suitable for treatment of previously untreated aluminium metal surfaces, and especially for extruded surfaces. 45

The process will usually be carried out by:

1. Cleaning the metal surface, preferably with an alkali cleaner;
2. Rinsing the cleaned metal surface with water;
3. Contacting the metal surface with an aqueous acidic treatment composition to form a coating

50 thereon; 50

4. Rinsing the coated metal surface with water;
5. Contacting the rinsed metal surface of step 4 with a post treatment solution; and
6. Drying the metal surface.

The zirconium ions can be introduced into the bath by any zirconium compound which is soluble in the aqueous acidic medium and which does not contribute deleterious components to the coating solution. 55

For example, suitable bath soluble zirconium compounds which can be employed include fluozirconic acid, ammonium and alkali metal fluozirconates, zirconium fluoride, zirconium nitrate, zirconium sulfate, or the like. The use of an alkali metal fluozirconate, such as, for example, potassium fluozirconate (K_2ZrF_6) is usually preferred in that it simultaneously introduces zirconium and fluoride ions into the bath composition. 60

The concentration of the zirconium ion can broadly range from as low as about 1 ppm to 5000 ppm and even higher with amounts ranging from about 4 ppm to about 100 ppm being preferred. A particularly satisfactory concentration of zirconium is about 50 ppm. 60

The source of hafnium ion employed in the present invention may be any hafnium compound which is soluble in the aqueous acidic medium and which does not contribute deleterious components to the coating bath. Examples of available hafnium compounds are set forth in the Handbook of Chemistry and 65

Physics, 55th Edition, CRC Press, Inc., Cleveland, Ohio (1974). Preferred sources of hafnium are hafnium oxide and acids or salts based upon hafnium or hafnium nitrate, fluoride or chloride. The hafnium compound should be included to provide a hafnium content of from about 1 ppm to about 5000 ppm. Preferably, the hafnium compound is present so as to supply hafnium in a concentration of between about 4 and about 100 parts per million, and more preferably about 50 ppm.

The source of titanium employed in the treatment solution can be any titanium compound which is soluble in the aqueous acidic medium and which does not contribute deleterious components to the coating bath. Examples of suitable titanium compounds include hexafluotitanic acid, titanium or titanyl sulfate, and ammonium or alkali metal-halide double salts such as potassium titanium fluoride. The use of salts containing both titanium and fluoride is usually preferred in that they simultaneously introduce both titanium and fluoride into the bath composition. The concentration of the titanium ion can broadly range from about 1 ppm to about 5000 ppm with from about 4 ppm to about 100 ppm being preferred, and more preferably about 50 ppm.

The treatment solution may contain only hafnium ions, or only zirconium ions or only titanium ions as well as mixtures thereof. When mixtures of the metal ions are employed, the total concentration of the mixture should be within the ranges as previously set forth, i.e. from about 1 ppm to about 5000 ppm and preferably from about 4 ppm to about 100 ppm. In accordance with a preferred embodiment of the present invention, the treating solution contains zirconium ions or predominantly zirconium ions.

The fluoride ion can be introduced into the composition in the form of a simple or complex fluoride compound such as hydrofluoric acid or a simple or bifluoride salt of an alkali metal or ammonium or as a complex fluoride acid or salt based upon an element such as boron, silicon, titanium, zirconium, and the like. The fluoride concentration can range from as low as about 1 ppm up to 6000 ppm or higher with amounts ranging from about 4 to about 100 ppm being preferred. A particularly satisfactory fluoride concentration is about 60 ppm. The particular fluoride ion concentration is preferably controlled in relationship to the quantity of hafnium and/or zirconium ions present. Preferably, when the metal ion is zirconium, the fluoride ion is present at a weight ratio of fluoride to zirconium of at least about 1.25:1. When the metal ion is hafnium, the fluoride ion is preferably present in a weight ratio of F:Hf of at least 0.64:1. The maximum fluoride ion concentration is controlled at a level below that at which an objectionable etching of the aluminium surface occurs. This maximum fluoride concentration is a function of the nature of the aluminium surface being treated, the temperature of the bath and the duration of the treatment time.

As previously indicated, the fluoride concentration in the bath is controlled in relationship to the concentration of the hafnium, and/or zirconium and/or titanium ions present so as to provide a stoichiometric ratio of at least 6 moles fluoride for each mole of the metal ion present. The free fluoride concentration in the bath is conveniently measured by a specific fluoride ion electrode in terms of millivolts (mv) which will vary depending upon the specific composition and concentration of the bath constituents and on the pH thereof. For any particular bath at a substantially constant pH, a correlation can readily be made of the millivolt reading and the free fluoride content which provides satisfactory bath operation. Such millivolt reading serves as a simple commercial control of the bath. For example, a satisfactory bath containing phosphate ions at a pH of about 3.7 is achieved by providing a free fluoride concentration to provide a millivolt reading of about -30 mv calibrated against a standard solution measured at 0 mv containing 4907 ppm H_2SO_4 (100%), 40 ppm F- added as NaF and 558 ppm F-added as NH_4HF_2 . The appropriate millivolt reading of the free fluoride concentration can readily be ascertained for any bath by simple experimentation to achieve the desired results.

It is also desirable to employ fluoboric acid in the bath in such instances to provide a reservoir source of free fluoride to supplement the free-fluoride concentration as it is consumed in the complexing of aluminium ions formed during the coating reaction.

In addition to the hafnium and/or zirconium ions and/or titanium ions and fluoride ions, the bath contains a bath soluble vegetable tannin compound. The chemistry of tannin agents is not completely understood at the present time. They include a large group of water soluble, complex organic compounds widely distributed throughout the vegetable kingdom. All have the common property of precipitating gelatin from solutions and of combining with collagen and other protein matter in hides to form leather. All tannin extracts examined contain mixtures of polyphenolic substances and normally have associated with them certain sugars. (It is not known whether these sugars are an integral part of the structure). For a discussion of tannins, see Encyclopedia of Chemical Technology, 2nd Edition, Kirk-Othmer; XII (1976) pp. 303-341 and The Chemistry and Technology of Leather, Reinhold Publishing Corporation, New York, pp. 98-220 (1958).

Tannins are generally characterized as polyphenolic substances having molecular weights of from about 400 to about 3000. They may be classified as "hydrolyzable" or "condensed" depending upon whether the product of hydrolysis in boiling mineral acid is soluble or insoluble, respectively. Often extracts are mixed and contain both hydrolyzable and condensed forms. No two tannin extracts are exactly alike. Principal sources of tannin extracts include bark such as wattle, mangrove, oak, eucalyptus, hemlock, pine, larch, and willow; woods such as quebracho, chestnut, oak and urunday, cutch and turkish; fruits such as myrobalans, valonia, dividivi, tera, and algarroballa; leaves such as sumac and gambier; and roots such as canaigre and palmetto.

The term "vegetable tannins" is employed to distinguish organic tannin such as those listed in the previous paragraph from the mineral tannin materials such as those containing chromium, zirconium and the like. Hydrolyzable, condensed, and mixed varieties of vegetable tannins may all be suitably used in the present invention.

5 When a vegetable tannin is employed, it is preferably present in an amount of at least 1 ppm, and more preferably, in an amount of at least 25 ppm up to the solubility of the compound in the bath with upper concentrations of about 500 ppm being satisfactory. Concentrations of about 70 ppm of the tannin compound are particularly satisfactory.

10 The treatment solution of the present invention must be adjusted in pH value to yield a pH on the acid side. Best results are obtained at pH values of less than 5 and the pH value is preferably at least 2. When the metal ion is hafnium or predominantly hafnium, the pH is preferably at least 2 and less than 3.5. When the metal ion in the treating solution is zirconium or predominantly zirconium, the pH is preferably from about 3.0 to about 4.5, most preferably from about 3.5 to about 4.0. When the metal ion is titanium or predominantly titanium, the pH is preferably from about 2.5 to about 4.0. Depending on the raw material compounds employed to supply the hafnium and/or zirconium and/or titanium and fluoride components, the pH value may be within an acceptable range without any further adjustment being necessary. On the other hand, if an adjustment of pH is necessary, any of the inorganic or organic compounds commonly used for pH adjustment may be employed. Among these materials are the mineral acids including hydrofluoric, sulfuric nitric and phosphoric acids, as well as the alkali metal and ammonium hydroxides, carbonates and bicarbonates, oxides and silicates.

20 The treatment bath also contains phosphate ions in an amount of about 10 up to about 200 ppm, preferably from about 25 to about 75 ppm with amounts of about 45 to about 55 ppm being particularly satisfactory. Suitable sources of phosphate ions for the solution include phosphoric acid and the various sodium, potassium or ammonium phosphate salts. The solution may optionally include a polyphosphoric acid, such as pyro-phosphoric acid, tripolyphosphoric acid, hexametaphosphoric acid or a sodium or potassium salt thereof; an organophosphate compound such as phytic acid; nitrodiethanoethylene sulfonic acid; phosphonate compounds such as 2-hydroxyethylmethacryl-1-acid, phosphonic acid, 2-ethylhexyl acid, ethane-1-hydroxy-1, 1-diphosphonic acid.

30 The sequestering agent of the treatment bath can be any conventional sequestering agent compatible with the other bath ingredients. Examples of suitable sequestering agents are ethylene-diaminetetraacetic acid (EDTA), alkali metal gluconates, alkali metal nitrates and the like. The sequestering agent is employed in an amount effective to avoid a detrimental amount of precipitation of aluminum in the treatment bath.

35 A particularly satisfactory bath composition according to the present invention contains zirconium ions in a concentration of about 50 ppm, a total fluoride ion concentration of about 180 ppm, a tannin concentration calculated on a weight equivalent basis to tannic acid of about 70 ppm, a phosphate ion concentration of about 50 ppm, and an effective amount of a sequestering agent.

40 Other adjuvants may optionally be included in the composition to modify one or more of the qualities of the coating obtained with the bath of the present invention. Among these possible adjuvants are nitrate compounds, and compounds containing titanium, lithium resinous materials. When employed, the adjuvants will normally be present in minor amounts.

45 In preferred processes of the present invention, aluminium surfaces are coated employing the hereinabove described aqueous acidic coating composition by contacting cleaned surfaces with the solution at a temperature of about room temperature (21°C) up to the boiling point of the solution, preferably temperatures ranging from about 37°C to about 71°C for periods of time ranging from about 0.1 seconds up to about 10 minutes with time periods ranging from about 2 seconds to about 1 minute being more typical. The formation of the coating is a function of concentration of the solution, temperature and contact time such that as the temperature and/or concentration of the solution is increased the contact time can be correspondingly reduced to achieve the requisite coating. Any conventional method of contacting the treating solution with the metal surface, e.g., spray, roll coating, immersion, or flooding, may be employed. The method of contacting the treating solution with the metal surface (by which terminology it is intended to include the method of contacting the metal surface with the treating solution) preferably involves sufficient combination of concentration of solution, temperature and treatment time to provide a coating of from about 2 to about 50, preferably 10 mg to about 40 mg per square foot (21 to 540, preferably 107 to 428, mg/m²) of aluminium surface.

55 After contacting the aluminium with the treatment solution, the treated aluminium is water rinsed and then contacted with a post-treatment solution such as that disclosed in U.S. 4,457,790. The post-treatment solution comprises an effective amount of a polymeric component referred to herein as a "post-treatment compound" and which is a soluble or dispersible post-treatment compound selected from polymers of formula 1 and acid salts thereof and mixtures thereof.

60 Preferably the compound has Z moieties present. Also preferably the post-treatment solution is an aqueous solution and Z moieties are present in sufficient amount that the compound is water soluble or water dispersible.

65 While the alkyl groups of the polymer backbone or chain in the above formula can be located in the ortho, meta, or para positions to the hydroxyl group on the aromatic ring of the phenol, monomer units

of the above general formula are preferably selected from the para and ortho forms.

It will be appreciated that in the polymeric form, the post-treatment compound of the present invention can comprise a plurality of different specific monomer units each of the above general formula. For example, a polymeric compound of this invention can have the general formula III where Y is defined as above (but is not hydrogen) and wherein A, B, C, and D can be from 0 to a number at which the polymer is not soluble or dispersible in the solvent under the conditions of use. A + B + C + D must be at least 2 and if the water is the solvent then the methylene amine moiety, the Z moiety as defined above, must be present in sufficient amount so that when neutralised with an acid, the polymer is water soluble or water dispersible. The particular amount as a molar percent needed for water solubility or dispersibility depends upon the molecular weight of the polymers as well as the particular R₄ through R₁₀ moieties in the polymer. Generally speaking, the molar percent of amino group or Z per phenolic group may vary from 10% to 200% and is usually 50% to 150%; there being one phenolic group per monomer.

The post-treatment compounds are derivatives of poly-alkenylphenol polymer. Examples of poly-alkenylphenols or substituted alkenylphenols useful in the present invention include isopopenylphenol, isobutenylphenol, dimethylvinylphenol and the like. Suitable derivatives having the above general formula can be made, for example, by the Mannich Reaction. For example, a poly-4-vinylphenol polymer can be reacted with formaldehyde and a secondary amine to yield a product which can be neutralised with an organic or inorganic acid to yield a water soluble or dispersible solution or emulsion of the post-treatment compound.

The molecular weight of the poly-alkenylphenol used in the preparation of derivatives claimed in the present invention can range from the dimer, or more usually low molecular weight oligomers of 360 to high molecular weight polymers of 30,000 or greater. The upper limit of molecular weight being determined by the functional limitation that the derivative therefrom be soluble dispersible.

The resulting derivatives of the formula set forth hereinabove will typically have a molecular weight of up to about 200,000, with molecular weights within the range of about 700 to about 70,000 being preferred. In the formula given for these derivatives, a typical upper value for "n" is about 850, with values of from about 10 to 300 being preferred. Similarly, the carbon chain lengths of the R₄ through R₁₀ substituents will typically be from about 1 to 18, with carbon chain lengths of from about 1 to 12 being preferred. It will, of course, be appreciated, that in each instance, a value for "n" and for the carbon lengths, as well as the percent of the "Z" moiety, will be selected which will provide the desired amount of solubility and/or dispersibility.

The post-treatment compounds are soluble in organic solvents and can be used as a post-treatment solution when dissolved in an organic solvent as, for example, ethanol. Advantageously, however, the post-treatment compounds can also be used in aqueous solution. To provide water solubility or water dispersibility of the compound, an organic or inorganic acid can be used for neutralization of the "Z" moiety thereof. Useful acids for this purpose are acetic acid, citric acid, oxalic acid, ascorbic acid, phenylphosphonic acid, chloromethylphosphonic acid; mono, di and trichloroacetic acid, trifluoroacetic acid, nitric acid, phosphoric acid, hydrofluoric acid, sulfuric acid, boric acid, hydrochloric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, and the like; alone or in combination with each other. The addition of water to the neutralized, overneutralized or partially neutralized treatment compounds mentioned above results in a water soluble or dispersible solution or emulsion of the polymer.

The pH of an aqueous post-treatment solution can vary from pH 0.5 to 12, but for practical purposes is usually kept between 2.0 to 8.0 both for the stability of the solution and for best results on the treated metal surface.

It is contemplated that the post-treatment compound will generally be used in a working solution at room temperature and at a dilute concentration of, for example, from about 0.001% to about 5% by weight. Practically speaking, a concentration of from about 0.005% to about .015% is preferred in a working solution. Also, it is contemplated that the post-treatment solution may comprise a pigment i.e., be a paint composition having a film forming component which can be the treatment compound itself, a solvent, and an organic or inorganic pigment.

Of course, the post-treatment solution can also comprise ingredients in addition to the post-treatment compound. For example, the post-treatment solution may optionally comprise, in addition to the post-treatment compound, from about 0.001% to about 1.0% of a metal ion selected from the group consisting of titanium, zirconium and hafnium ions and mixtures thereof. It will be appreciated that these ions are of Group IV B transition metals of the Periodic Table of the Elements and may be provided in aqueous solution by the addition of their water soluble acids or salts, for example, hexafluorotitanic acid, hexafluorozirconic acid, hexafluorohafnic acid, or the nitrate, sulfate, fluoride, acetate, citrate, and/or chloride salts. Use of such additional metal ions can improve both the effectiveness or performance of the treatment solution in use and also can reduce the time of application of treatment solution to the metal surface to as short a time as one second.

Still other optional ingredients may be employed in addition to, or instead of, the aforementioned metal ions. For example, in addition to the post-treatment compound and a metal ion selected from this group consisting of titanium, zirconium, and hafnium ions and mixtures thereof, the post-treatment solution can comprise from about 0.01% to about 4.0% of ingredients selected from the group consisting of thiourea, alkyl or aryl thiourea compounds, tannic acid, vegetable tannins or gall tannins and mixtures

thereof. Examples of suitable ingredients include methyl, ethyl or butyl thiourea, wattle, mangrove or chestnut tannins, oak gall tannin, and valonea acorn cup extract.

Application of the post-treatment solution to the treated metal surface can be carried out by any conventional method. For example, the post-treatment solution can be applied by spray coating, roller coating, or dipping. The temperature of the solution applied can vary over a wide range, but is preferably from 70°F to 160°F. The time of contacting the aluminum surface can vary from 1 second to 1 hour. After application of the treatment solution to the metal surface, the surface can optionally be rinsed, although good results can be obtained without rinsing after treatment. For some end uses, for example, in electrocoat paint application, rinsing may be preferred.

Next, after being contacted with the post-treatment solution and optionally rinse water, the treated surface is dried. Drying can be carried out by, for example, circulating air or oven drying. While room temperature drying can be employed, it is preferable to use elevated temperatures to decrease the amount of drying time required.

After drying, the treated aluminum surface is then ready for painting or the like. The surface is suitable for standard paint or other coating application techniques such as brush painting, spray painting, electrostatic coating, dipping, roller coating, as well as electrocoating. As a result of the process of the present invention, the aluminum surface has excellent paint adhesion and corrosion resistance characteristics.

EXAMPLE I

Treatment solution

A concentrate was prepared to contain:

	Ingredient	% by weight	
	K ₂ Zr F ₆	0.624	
	NH ₄ HF ₂	0.081	
	42°BeHNO ₃	0.74	
	49% HBF ₄	0.96	
	NH ₄ H ₂ PO ₄	0.22	
	Versene (EDTA)	0.078	
	dried chestnut extract (vegetable tannin)	0.27	
	deionized water	to 100	

The above concentrate was diluted by the addition of tap water and the pH adjusted by the addition NH₄ HCO₃ to about 3.75 to provide an aqueous treatment solution as follows:

	Ingredient	g/L	
	K ₂ Zr F ₆	0.16	
	NH ₄ HF ₂	0.02	
	42°BeHNO ₃	0.19	
	49% HBF ₄	0.25	
	NH ₄ H ₂ PO ₄	0.056	
	Versene (EDTA)	0.02	
	dried chestnut extract (extract vegetable tannin)	0.07	

Post-treatment solution

100 lbs. of Proposol P solvent (Union Carbide) was charged into a 100 gallon stainless steel reactor containing a turbine blade, nitrogen sparge and condenser. Gentle heating to 50°C was started, and 80 lbs. of poly-4-vinylphenol polymer of a molecular weight of 5000 was slowly added to the solvent with good stirring. After all of the polymer was added, the reactor was closed and heated to 80°C to aid in dissolving the remaining polymer. The reactor was then cooled to 60°C and 50 lbs. of N-Methylaminoethanol and 100 lbs. of deionized water was added. Then, over one (1) hour, 54.1 lbs. of 37% formaldehyde solution was added while maintaining the temperature at 60°C to ±2°C. The reactor was then heated for 3 hours at 60°C and 21.8 lbs. of 75% Phosphoric acid was added and the mixture was diluted to 10% solids with deionized water to yield a stable solution.

The above solution was diluted with deionized water and pH adjusted to about 4.25 by the addition of 25% phosphoric acid to provide a concentrate as follows:

<i>Ingredient</i>	<i>Percent by Weight</i>
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5	Proposal P solvent	0.95	5
	poly-4-vinylphenol	0.53	
	N-methylethanol amine	0.33	
	37% formaldehyde solution	0.36	
	75% phosphoric acid	0.42	

10 The above concentrate was then diluted to 1% v/v to provide a post-treatment solution as follows: 10

<i>Ingredient</i>	<i>g/l</i>
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15	Proposol P solvent	0.0095	15
	poly-4-vinylphenol	0.0053	
	N-methylethanol amine	0.0033	
	37% formaldehyde solution	0.0036	
	75% phosphoric acid	0.0042	

20 20

Extrusion aluminum panel were cleaned with an alkaline cleaner, rinsed with tap water and treated with the above treatment solution by spraying the treatment solution having a temperature of 125°F onto the panel for 30 seconds, rinsed with tap water and then treated with the above post-treatment solution by spraying the post-treatment solution having a temperature of 125°F onto the panel for 30 seconds. Then the panels were hot air dried and painted with a PPG (Pittsburgh Plate and Glass), medium solids, low cure paint (Duracron 100). The panels were then subjected to accelerated testing and found to exhibit excellent paint adhesion and corrosion resistance.

30 **EXAMPLE II** 30
A treatment solution is prepared in deionized water to contain:

<i>Ingredient</i>	<i>g/l</i>
60% H_2TiF_6	1.48
70% HF	1.12
26 Be°NH ₄ OH	3.0
NH ₄ H ₂ PO ₄	2.2
dried chestnut extract (vegetable tannin)	0.93
Rayon grade NaOH	0.045
50% tris Nitro	1.2
Versene (EDTA)	0.08
NH ₄ HCO ₃	to pH 3.75

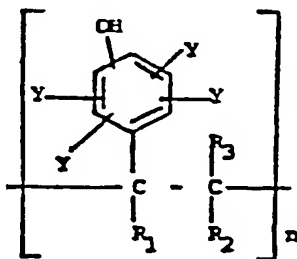
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Extrusion aluminium panels are cleaned, rinsed, treated, rinsed, post-treated, air dried and painted as in Example I except the above treatment solution was substituted for the treatment solution of Example I. The panels have excellent paint adhesion and corrosion resistance characteristics.

50 **EXAMPLE III** 50

The procedure of Example II is repeated with similar results except 0.85 g/l of H_2HfF_6 is substituted for the 1.48 g/l of 60% H_2TiF_6 in the treatment solution of Example II and the pH of the treatment solution is adjusted to about 3.0 instead of 3.75.

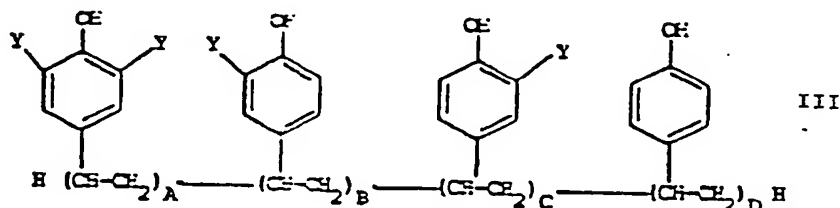
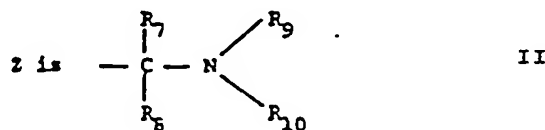
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CLAIMS

1. A process of treating an aluminium surface comprising sequentially contacting an aluminium surface with:
 - (1) an aqueous acidic treatment solution comprising an effective amount of:
 - (A) dissolved metal ions selected from the group consisting of hafnium, zirconium, titanium and mixtures thereof;
 - (B) phosphate ions;
 - (C) fluoride ions;
 - (D) a bath solution vegetable tannin compound;
 - (E) a sequestering agent; and
 - (2) a post-treatment solution comprising an effective amount of a soluble or dispersible compound selected from the group consisting of a polymer having general formula I, acid salts thereof and mixtures thereof wherein
 - R₁ to R₈ are hydrogen or an alkyl group having from 1 to about 5 carbon atoms;
 - each Y is hydrogen, Z, CR₄R₅OR₆, CH₂Cl, or an alkyl or aryl group having from 1 to 18 carbon atoms;
 - Z is a group of general formula II, and the groups R₄ to R₁₀ are each hydrogen, or an alkyl, aryl, hydroxy-alkyl, amino-alkyl, mercapto-alkyl or phospho-alkyl moiety, and are each of a carbon chain length below that at which the compound or its acid salt, is not soluble or dispersible; and
 - n is at least 2 but below a number at which the polymer or its acid salt is not soluble or dispersible.
2. A process according to claim 1 wherein the treatment solution has a pH of from about 2.0 to about 5.0, the metal ion, phosphate ion fluoride ion and vegetable tannin are present in amounts of at least 1 ppm of each, sufficient when contacted with the metal surface, to impart corrosion resistance to the metal surface, and the sequestering agent is present in an amount effective to prevent detrimental precipitation of aluminium from the solution; and the post-treatment solution is an aqueous solution, and Z moieties are present in a molar percent of from 10% to 200% per phenolic group.
3. A process according to claim 1 or claim 2 wherein the metal ion is predominantly zirconium and the pH is from 3.0 to 4.5.
4. A process according to claim 1 or claim 2 wherein the metal ion is predominantly hafnium and the pH is from 2 to 3.5.
5. A process according to claim 1 or claim 2 wherein the metal ion is predominantly titanium and the pH is from 2.5 to 4.0.
6. A process according to any preceding claim wherein the compound of Formula I comprises the reaction product of a poly-4-vinylphenol, formaldehyde and a secondary amine.
7. A process according to any preceding claim wherein the compound of Formula I is present in an amount of from about 0.01% to about 5.0%.
8. A process according to any preceding claim wherein the treatment solution is contacted with the aluminium surface for a time sufficient to provide a coating thereon of from 21 to 540 mg/m² of aluminium surface.
9. A process according to any preceding claim wherein subsequent to step (2) a paint is applied to the aluminium surface.
10. A process according to any preceding claim wherein the vegetable tannin compound is chestnut extract.

11. A process according to any preceding claim wherein the metal ion is present in an amount of from 4 ppm to 100 ppm, the fluoride ion is present in an amount of from 4 ppm to 100 ppm, the tannin is present in an amount of from 25 ppm to 500 ppm, the phosphate is present in an amount of from 10 ppm to 200 ppm and the sequestering agent is present in an amount effective to prevent detrimental precipitation of metal ions in said treatment solution.

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